Supporting information

Non linear magnetic behaviour around zero field of an assembly of superparamagnetic nanoparticles

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Multiparametric Testing

In an attempt for multiparametric feasibility, two SPM probes : lab-made γ-Fe_2O_3 nanoparticles and commercial Estapor beads (1020/50, Merck), are mixed at different ratios. The iron concentration of the two ferrofluids was adjusted in order to obtain MIAplex® signatures at isointensity. Fig. S1A shows the MIAplex® signatures of the two kinds of particles.
Fig. S1B-D shows the experimental MIAplex® signatures measured by mixing the two kinds of particles in various proportions and the corresponding calculated curves. A rather good agreement is obtained between experimental and calculated curves. This confirms the high sensitivity of measuring $d^2B(H)/dH^2$ for characterization and separation purpose.

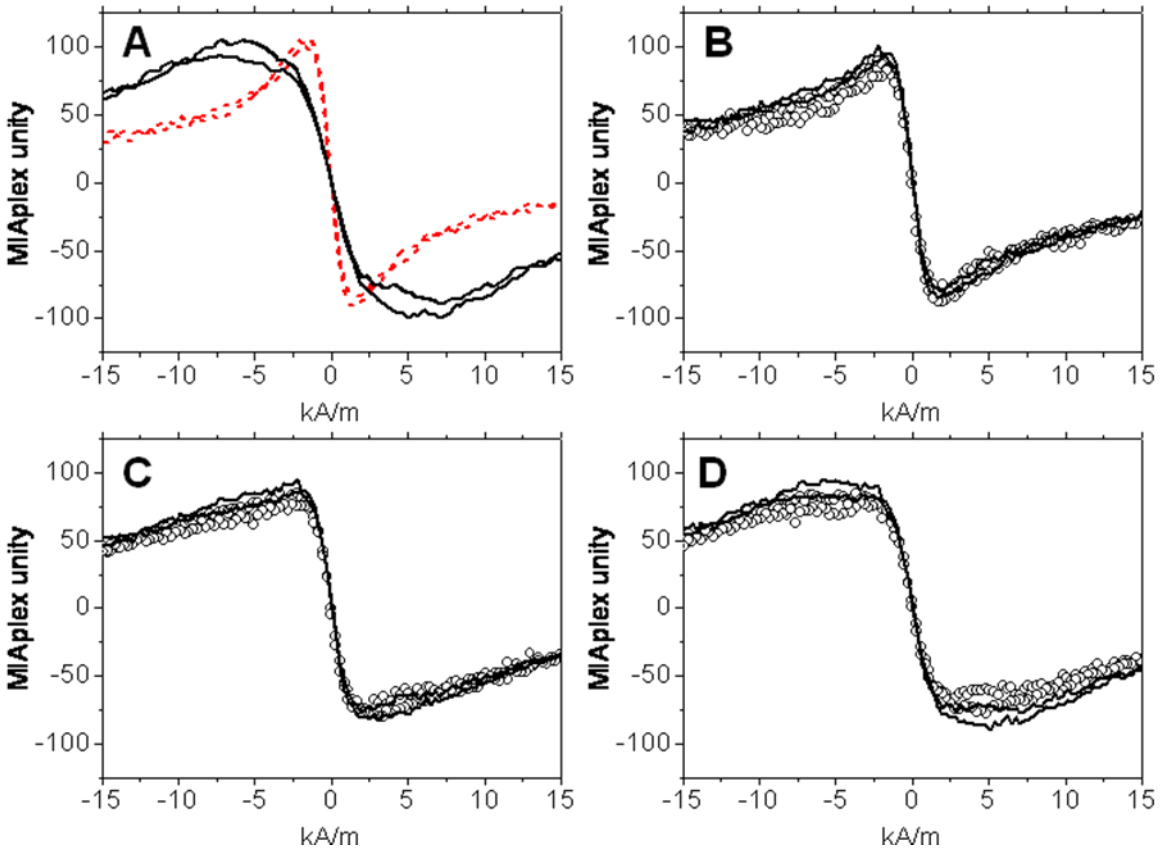

Figure S1: A : MIAplex® signature for nanoparticles (dashed line) and Estapor beads (solid line). Experimental (open circles) and calculated (solid line) curves for 75%-25% (B), 50%-50% (C), and 25%-75% (D) nanoparticles-Estapor mixtures.

Synthesis and characterization of γFe_2O_3 nanoparticles

Sodium n-dodecyl sulfate (99%, Alfa Aesar), dimethylamine solution (40%, Fluka), Iron (II) Chloride Tetrahydrate (Sigma Aldrich) were used as received. Water is purified with a Millipore system (resistivity 18.2 MΩ.cm).
Concerning lab-made nanoparticles, they are synthesized according to a procedure already described. Briefly, non coated γFe_2O_3 particles were synthesized by reaction of ferrous dodecyl sulfate with dimethylamine in water for two hours at 28°C[1]. The nanocrystal surface is then functionalized with 5-

hydroxy-5,5-bis(phosphono)pentanoic acid, which allows a good dispersion in water of the nanoparticles. The nanoparticles surface is characterized via infrared spectroscopy (Fig. S1).

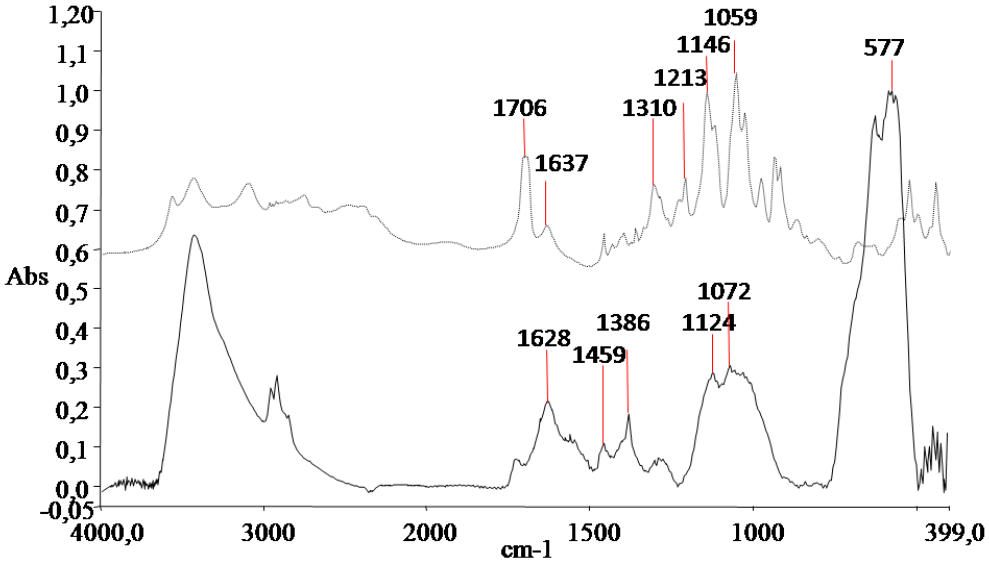

Figure S2: Infrared spectra of free 5-hydroxy-5,5-bis(phosphono)pentanoic acid (HMBP) (dotted line) and 10nm γFe_2O_3@HMBP nanoparticles (solid line).

The spectrum of free HMBP molecule contains peaks at 1706cm^{-1} (C=O), 1637cm^{-1} (carboxylic C-O), 1309 and 1213cm^{-1} (δCH_2), 1146 and 1059cm^{-1} (P-O). The spectrum of coated nanoparticles presents a very intense band at 577cm^{-1} attributed to Fe and a large intense vibration band between 1150 and 950cm^{-1} which corresponds to the P-O absorption band. Compared to free molecule, this modified band indicates that the molecule is bonded at the surface of the particle via the hydroxymethylene-bisphosphonate terminal function. The coating rate has been quantified via the P-O area band[1] and is evaluated as about 1500 HMBP molecules per nanoparticle.

Nanoparticles crystal size and structure were characterized by X-ray diffraction (XRD) and Transmission Electron Microscope (TEM). XRD pattern (Fig. S2 and S3) was measured with an X-ray powder diffractometer model X'Pert PRO, MPD, PANalytical, Almelo, the Netherlands, CoKα beam in Bragg Brentano geometry (y/y) was used combined with a fast detector based on real time multiple strip technology (X'Celerator). Crystal XRD size was determined with the Scherrer formula. TEM images were obtained using a FEI CM10 Microscope and samples were prepared by depositing a drop of nanoparticles suspension on carbon coated copper grids placed on a filter paper.

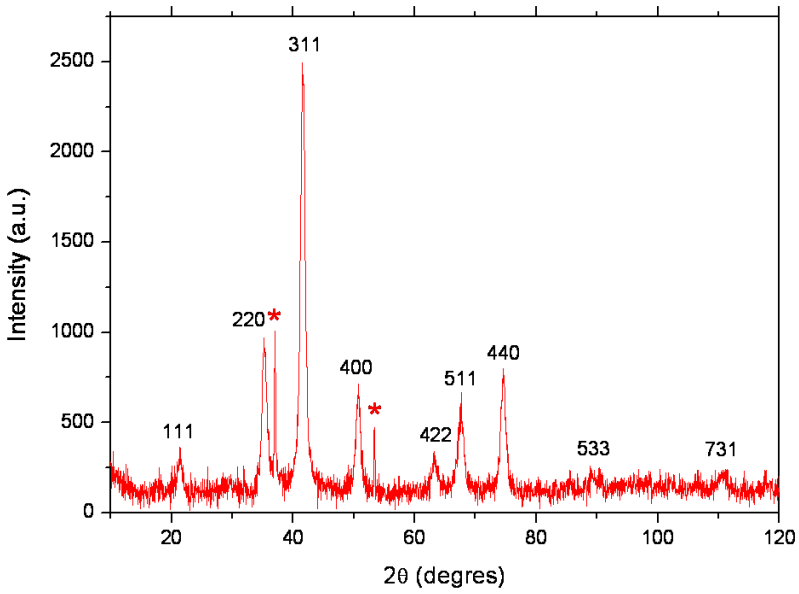

Figure S3: XRD pattern 10nm γFe_2O_3@HMBP nanoparticles.

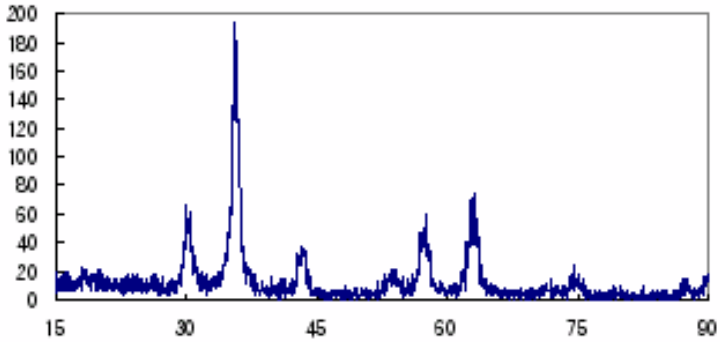

Figure S4: XRD pattern of Ferrotec Nanoparticles

The stars Figure S3 indicate the presence of NaCl residue. Phases identified are maghemite γFe_2O_3 and magnetite Fe_3O_4 (EVA software (version 13, Bruker-AXS, Karlsruhe, Germany, 1996–2007) and JCPDS-International Centre for Diffraction Data Powder Diffraction File (PDF-2, JCPDS-ICDD, Newtown Square, PA)). Crystal size is determined via the Scherrer equation and is 9.9nm.

The median diameter d_0 and standard deviation w are deduced from TEM data measurements, simulating the diameter d distribution with a lognormal function g(d) described in equation (1).

$$g(d) = \frac{1}{\sigma d\sqrt{2\pi}} \exp\left(-\frac{\left(\ln\frac{d}{d_0}\right)^2}{2\sigma^2} \right) \quad (1)$$

The parameter σ is related to the standard deviation w by the relation (2).

$$\sigma = \sqrt{\ln\left(1+\left(\sqrt{1+4\left(\frac{w}{d_{med}}\right)^2}-\frac{1}{2}\right)\right)} \approx \sqrt{\ln\left(1+\left(\frac{w}{d_{med}}\right)^2\right)} \quad (2)$$

Magnetic properties of γFe_2O_3 nanoparticles

Magnetic properties were measured using a superconducting quantum interference device (Quantum Design SQUID Magnetometer MPMS-5T) at 300 K and the MIAplex® technology. Samples measured with SQUID are liquid suspensions in water, 0.5wt%, conditioned in silicone capsules supplied by Plastem S.A. Concerning the MIAplex®, samples are also liquid suspensions in water 0.5wt% and 2wt%, conditioned in 500µL Eppendorf.

The saturation magnetization is obtained by the extrapolation of the plot of magnetization vs the inverse of the field at the origin[2] (Fig. S4).

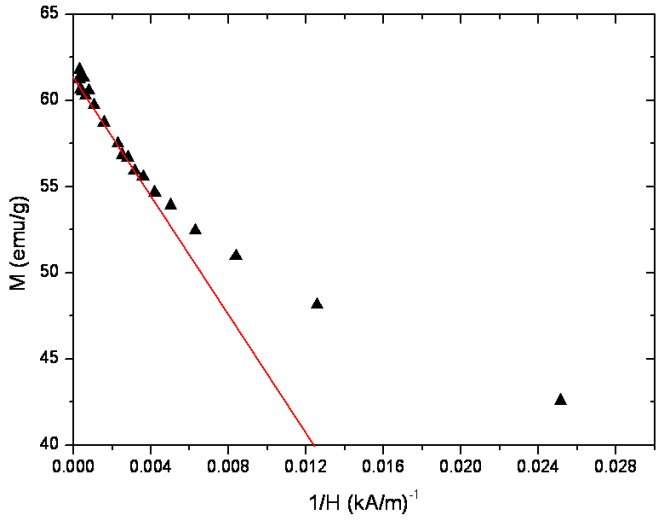

Figure S5: Magnetization M as function of 1/H.
The red line is the asymptote when 1/H tends to zero. The intersection between this asymptote and y-axis is the experimental saturation magnetization M_{sat}.

Considering a core-shell system, the spin canting thickness e and the corresponding magnetic size (d_0-2e) are deduced from the equation (2)[3].

$$M_{sat} = M_{satbulk} \times \left(\frac{d_0 - 2e}{d_0} \right)^3 \qquad (2)$$

For the lab-made nanoparticles with d_0 = 10.5nm as TEM diameter and M_{sat} = 61emu/g, we calculate a magnetic size of d_m = 9.6nm, corresponding to a non magnetic layer of e ≈ 0.45 nm. We estimate the contribution of the shell in the total volume of the particles from the equation (3).

$$\%(V_{shell}) = 100 \times \frac{V_{shell}}{V_{cristalline}} = 100 \times \frac{V_{cristalline} - V_{magnetic}}{V_{cristalline}} = 100 \times \frac{{d_0}^3 - {d_m}^3}{{d_0}^3} \qquad (3)$$

We so obtained a shell contribution of 24% of the particle volume.

The Langevin model of superparamagnetism[4] can be used to describe the non-linear magnetization curve of the nanoparticles, assuming that particles do not interact, by the equation (4).

$$\frac{M}{M_{sat}} = \coth\left(\frac{\nu \rho M_{sat} \mu_0 H}{k_b T} \right) - \frac{k_b T}{\nu \rho M_{sat} \mu_0 H} \qquad (4)$$

ν is the volume of the magnetic core, ρ is the particle density (4900kg.m^{-3} for maghemite), M_{sat} (emu.g^{-1}) is the saturation magnetization of the particle, T is the sample temperature in Kelvin (taken to be 300 K), μ_0 is the permeability of vacuum ($4\pi \times 10^{-7}$ H.m^{-1}), H is the applied field (in A.m^{-1}) and k_b is the Boltzmann constant, 1.38×10^{-23} J.K^{-1}. As to model the experimental magnetic data, we have used the Langevin equation weighted by a lognormal function (equation 1).
The experimental curves at high and medium magnetic field ranges are fitted with 1 Langevin equation weighted by log-normal distribution.
At low magnetic field range, the experimental curve are fitted with the sum of 2 Langevin equations weighted by log-normal distribution and corresponding to separate contributions.

The second derivative of the magnetization fit at high and medium magnetic field ranges is compared with the MIAplex® signature (Figure S5).

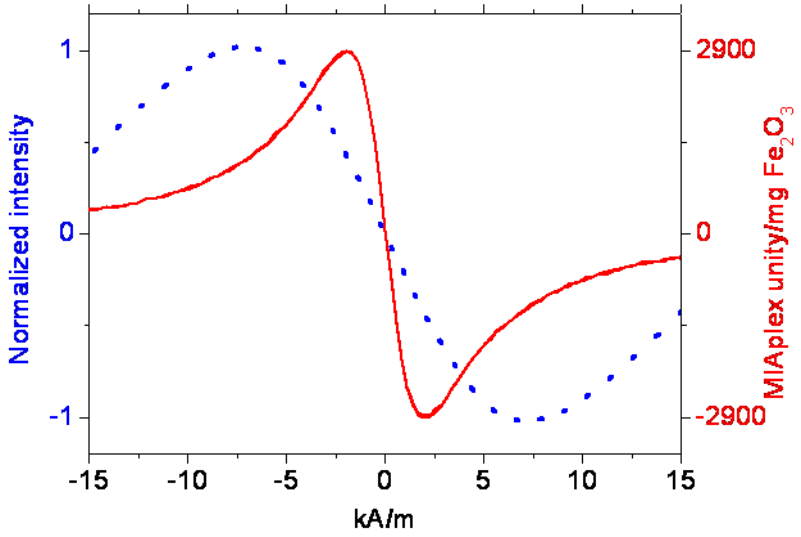

Figure S6: Second derivative of the magnetization fit at high and medium magnetic field **range (dotted line) superposed with the MIAplex® signal (solid line).**
The second derivative of the high and medium magnetic field magnetization fit presents a peak-to-peak line width in field ΔH_{pp} = 14.4 ± 0.2 kA.m^{-1} which is about 3.7 times bigger than the MIAplex® signature (ΔH_{pp} = 3.9 ± 0.1 kA.m^{-1}).

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2. Caizer, C. Saturation magnetization of [gamma]-Fe2O3 nanoparticles dispersed in a silica matrix. *Physica B: Condensed Matter* **327**, 27-33 (2003).
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4. du Trémolet de Lacheisserie, E. Magnétisme Fondements Vol. I. (Grenoble Science, Grenoble; 2000).